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Synthesis of Inorganic Polymers as Glass Precursors and for Other Uses. Preceramic Block or Graft Copolymers as Potential Precursors to Nanocomposite Materials

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Preceramic block or graft copolymers may offer entrée into nanocomposite ceramics provided the two homopolymers are immiscible and one can carefully control the size of the blocks or grafts. We are exploring the possibility of making copolymers from methylsilsesquioxane, $-[MeSi(O)_{1.5}]_x-$ (SiO), a precursor to "black glass" and the polysilazane, $-[MeHSiNH]_x-$ (SiMe), a precursor to silicon carbide nitride. Our initial efforts have been directed towards delineating the chemical transformations that SiO, prepared by room temperature catalytic redistribution of $-[MeHSiO]_x-$ using Cp_2TiMe_2 as the catalyst (0.1 wt %), undergoes as it is heated to 900°C in N_2. We find that although Cp_2TiMe_2 will not catalyze the redistribution of SiMe at room temperature; in the presence of even small amounts of $-[MeHSiO]_x-$, it is an active catalyst precursor and a copolymer can be formed. Spectral and chemical composition studies on the pyrolysis products of the copolymers and SiO are described.
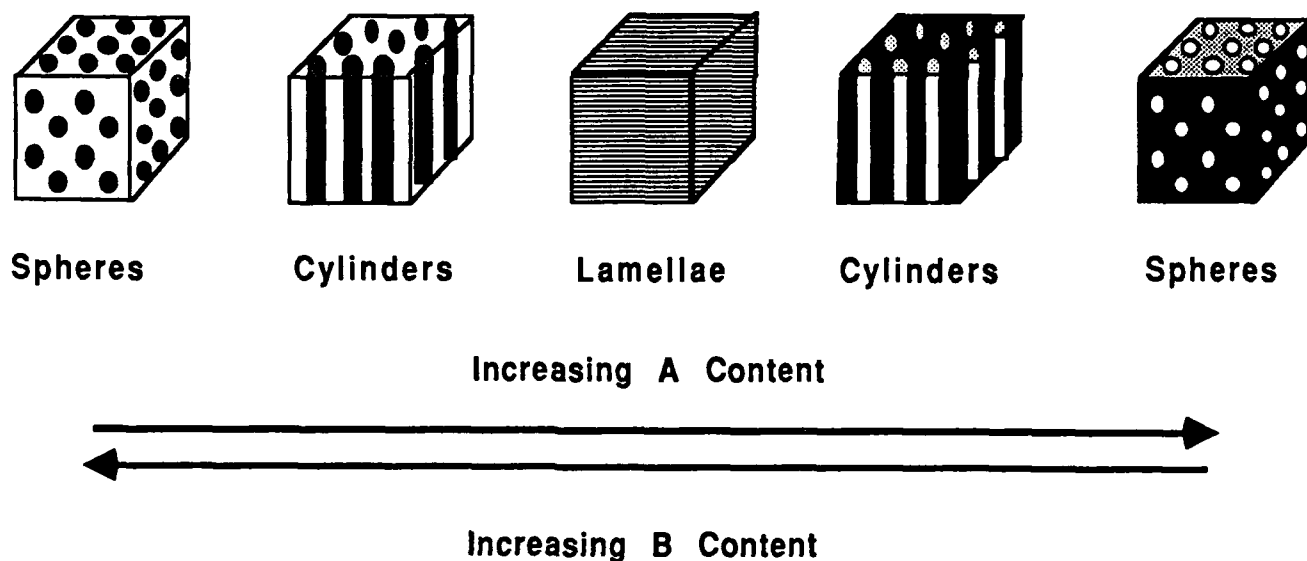
1. Introduction

The alloying or blending of one polymer with another is often used as a means of enhancing the physical and chemical properties of one or both polymers. Mixing is obtained by dissolution in a common solvent or by melt-mixing. This "co-mingling" of properties is effective only if the two polymers are compatible and do not segregate (on a macroscopic level) upon heating, with time, or segregate only under a specific (narrow) set of

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conditions.

Segregation in polymer blends or alloys can sometimes be avoided through the synthesis of block or graft copolymers wherein oligomeric chains of polymer A are chemically bonded to chains of polymer B. However, if the physical properties of A and B are quite disparate, then segregation can occur on a mesoscopic (nano) scale. In some instances, mesoscopic segregation can be beneficial, especially for "toughening" purposes.

For example, the block copolymerization of A with B or grafting of A to B, can lead to the formation of unique, three dimensional microstructures, as illustrated by Scheme 1[1]. Thus, if A is the minority phase in a block or graft copolymer of A and B, then one obtains a segregated structure, as shown below, in which spheres of A form in a matrix of B. The converse is true if small quantities of B oligomers are copolymerized with A oligomers. As the mole fraction of A oligomers

| Spheres | Cylinders | Lamellae | Cylinders | Spheres |

Increasing A Content

Increasing B Content

Scheme 1. Effect of Changes of Composition on the Microstructure of a Block Copolymer.

increases relative to B oligomers then one obtains progressively: spheres, cylinders and then lamellar structures when A ≈ B. These structures offer considerable potential for "toughening" provided certain design criteria are

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met[1].

The diameter and definition of the spherical and cylindrical microstructures are controlled by the polymer, the chain lengths and the polydispersity of the minority component. Likewise, the thickness and definition of each lamella is controlled by the number of monomer units in the chain segments of A and B as well as the polydispersity. Furthermore, A must be immiscible in B. If these design criteria are met, it should be possible to tailor the microstructures of block or graft copolymer shapes and thereby obtain precise control of the physical and mechanical properties of the resultant piece.

Extension of the concept of tailored block or graft copolymers to preceramic polymers, offers the unique opportunity to fabricate ceramic shapes wherein one can control the size, configuration and distribution of heterogeneities in the ceramic body by controlling the nanostructural features of the precursor polymer. Thus, small amounts of precursor oligomer A, copolymerized with oligomers of precursor B should lead to ceramics, following pyrolysis, that have approximately spherical reinforcing heterogeneities. This assumes that the oligomers of A are not miscible with B and that their chain lengths and molecular weights are narrowly defined. It also assumes that segregation is maintained during pyrolysis.

To our knowledge, no one has attempted to develop preceramic block or graft copolymers for the express purpose of introducing controlled heterogeneities into the resultant ceramic product. Seyferth et al.[2] have synthesized -[(MeSiH)$_a$(MeSi)$_b$-(Me$_3$SiNH)$_c$(MeSiN)$_d$(MeHSiNMe)$_e$]$_n$- graft copolymers to adjust the composition (SiC:Si$_3$N$_4$) of the final ceramic product. However, with the exception of Seyferth et al., little has been done to develop systems of mixed preceramic polymers either by chemical linkage (grafting or copolymerization) or by physical mixture, despite the potential for forming nanocomposite materials.

The long term objective of the work discussed here is to explore the use of preceramic copolymers as a means of preparing ceramic materials with controlled heterogeneities--nanocomposite ceramics. However, to achieve this objective it is first necessary to develop two distinct preceramic polymer systems wherein we can exert control of both the macromolecular properties (degree of polymerization, polydispersity, rheology) and pyrolytic selectivity to specific ceramic products. It will

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also be necessary to establish that physical mixtures and then copolymers of these preceramics will segregate and will, when pyrolyzed, give ceramic products that maintain the preceramic segregation. Furthermore, we must also develop methods of characterizing both the preceramics and the expected amorphous ceramic products so that we can identify the individual product phases. Finally, the choice of both preceramics must be such that on pyrolysis they do not react to form a third ceramic material.

To this end, we are exploring the use of two types of preceramic polymers. One, based on $-[MeHSiO]_x-$, when catalytically polymerized and pyrolyzed to 900°C, gives "black glass" which consists of silica (79% by mole fraction), SiC (20%) and carbon (10%). The second preceramic is the nitrogen analog, $-[MeHSiNH]_x-$ (SiMe), which when pyrolyzed to 900°C gives an amorphous ceramic with an apparent ceramic composition of Si_3N_4 (65% by mole fraction), SiC (25%) and carbon (10%). In this paper, we discuss our preliminary studies on the pyrolysis and characterization of the black glass precursors, and results of our studies on pyrolysis of that precursor with the SiMe polysilazane, $-[MeHSiNH]_x-$. The synthetic and experimental details will be presented elsewhere.

2. Results and Discussion

Alkyl silsesquioxanes, $-[RSi(O)_{1.5}]_x-$, prepared by sol-gel processing of alkylsiloxanes, $RSi(OEt)_3$, have been studied by Fox et al.[3] as

$$RSi(OEt)_3 + 1.5H_2O \xrightarrow{\text{catalyst = acid}} 3EtOH + -[RSi(O)_{1.5}]_x- \qquad (1)$$
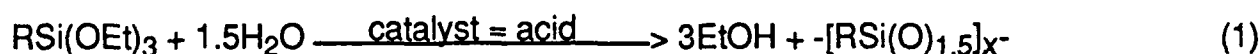
precursors to silicon carbide powders and to silicon carbide reinforced black glass [reaction (1)]. Kamiya et al.[4] have recently described the use of methyl silsesquioxane as a precursor for the processing of nitrided glass fibers. Zhang and Pentano[5] are currently exploring the utility of black glasses as a matrix for the fabrication of graphite fiber composites.

Our recent discovery[6] that dimethyltitanocene derived catalysts can be used to catalyze the redistribution of hydridosiloxanes, reaction (2), at room temperature, prompted us to consider using the same system, as in reaction (3), to produce the silsesquioxane, $-[MeSi(O)_{1.5}]_x-$ from

$$MeHSi(OEt)_2 \xrightarrow{Cp_2TiMe_2/RT} MeSiH_3 + MeSi(OEt)_3 \qquad (2)$$

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$$-[\text{MeHSiO}]_x- \xrightarrow{\quad \text{Cp}_2\text{TiMe}_2\ /\text{RT} \quad} 1/3x\text{MeSiH}_3 + -[\text{MeSi(O)}_{1.5}]_{2/3x}- \qquad (3)$$

$-[\text{MeHSiO}]_x-$.

Furthermore, the tetrameric and pentameric cyclomers of $-[\text{MeHSiO}]_x-$ or well defined (by D.P. or M_n) linear chain analogs are commercially available. This suggested that these species, when used in conjunction with reaction (3), might serve as a potential second preceramic system with the well studied SiMe polysilazane system[2,7-9] to test the feasibility of the block copolymer approach to nanocomposite structures. Finally, we found that the siloxane precursor was not miscible with either $-[\text{MeHSiNH}]_x-$ or the isostructural $-[\text{H}_2\text{SiNMe}]_x-$[9].

Methylsilsesquioxane

Our first objective was to define the pyrolysis characteristics of the methylsilsesquioxane, $-[\text{MeSi(O)}_{1.5}]_x-$, produced in reaction (3). We have studied the chemical evolution of $-[\text{MeSi(O)}_{1.5}]_x-$ during pyrolysis from 25°C to 1000°C by chemical analysis and diffuse reflectance infrared fourier transform spectroscopy (DRIFTS). A good portion of this work will be reported at a later date; however, the DRIFTS data shown in Figure 1 are pertinent to the present work. The most useful absorption bands are those that correspond to ν O-H (3250-3600 cm^{-1}), ν C-H (2750-3000 cm^{-1}) and ν Si-H (2100-2230 cm^{-1}). The starting polymer has no bands attributable to an O-H stretching frequency, as expected, given that reaction (3) does not involve hydrolysis.

Insert Figure 1

As the polymer is heated from 25-600°C, very little change is observed in the shapes of these peaks; however, the Si-H bonds diminish with increasing temperature. By 600°C, the peak corresponding to ν Si-H disappears and some broadening of the C-H peak is observed as the polymer undergoes extensive crosslinking which "freezes" individual polymer chain segments in multiple conformations. What is extremely intriguing is that as the polymer is heated to 800°C, Si-H peaks reappear at 2200 and 2250 cm^{-1}. Coincident with the reappearence of Si-H bonds, we also see the formation of a broad peak corresponding to ν O-H. This was verified by

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exchange with D_2O, which shifts a good portion of the O-H stretching vibrations to 2400 cm^{-1} (v O-D).

The disappearence of Si-H bonds in the 600°C intermediate suggests that this material contains only Si-O, Si-C, C-H, and possibly Si-Si bonds. Therefore, we must conclude that the reappearence of Si-H bonds and the appearence of O-H bonds in the 800°C intermediate results as a consequence of the reaction of C-H bonds with Si-O bonds. We assume that Si-C bonds are formed coincident with the formation of the Si-H and O-H bonds. This then is evidence for the first chemical steps in the carbothermal reduction of silica by hydrocarbons. In addition, it also partially delineates the reaction pathway(s) whereby SiC is formed during the pyrolysis of -[MeSi(O)$_{1.5}$]$_x$-. Of primary importance is the fact that we have a partial picture of the decomposition pattern of the -[MeSi(O)$_{1.5}$]$_x$- polymer for use in characterizing the decomposition patterns of any potential copolymer.

SiMe Polysilazane

A number of researchers[2, 7,10] have previously shown that pyrolysis of the SiMe polysilazane, -[MeHSiNH]$_x$-, leads to the formation (at 900°C in N_2) of mixtures of silicon nitride, silicon carbide, and carbon. Typical DRIFTS spectra are shown in Figure 2[10]. Unlike the DRIFTS studies of the -[MeSi(O)$_{1.5}$]$_x$- pyrolytic intermediates, the SiMe intermediates do not exhibit any noteworthy chemical changes apart from the typical broadening of the v N-H and v C-H peaks as the polymer becomes progressively more crosslinked (200-400°C), chars (400-600°C), and eventually becomes a true ceramic material(>600°C). One difference between the SiMe spectra and the SiO spectra is that the v Si-H peaks diminish but never really disappear even at 800°C.

Insert Figure 2

Based on the spectra shown in Figures 1 and 2, it is not clear that we can use DRIFTS as the sole analytical tool with which to follow the chemical evolution of physical mixtures of the two preceramics or true copolymers. Furthermore, studies[11,12] on the pyrolysis of polymers of the general type, -[Me(NH)$_{0.5}$SiO]$_x$- under N_2 and especially NH_3, show that the major product formed is silicon oxynitride (Si_2ON_2). Thus, it is quite

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possible that Si_2ON_2 will be one of the products formed upon pyrolysis of mixtures of the two preceramics.

However, our initial objectives are: (1) to establish whether or not it is feasible to form copolymers from the two precursors we have chosen to study and; (2) to determine whether or not we can obtain defined microstructures from physical mixtures or copolymers of two inorganic polymers. Furthermore, even if these precursors do eventually produce silicon oxynitride upon pyrolysis, we are interested in following the kinetics of formation as a function of temperature especially from segregated phases.

With this in mind, we sought to establish the reactivity of the SiMe polysilazane with Cp_2TiMe_2. After repeated tries, we were unable to obtain any type of catalysis. Thus, we assumed that the addition of catalytic amounts of Cp_2TiMe_2 to well-stirred physical mixtures of the SiMe polysilazane ($M_n \approx$ 500-600 D) and -[MeHSiO]$_x$- ($M_n \approx$ 2000 D) would cause only the latter to polymerize. We also assumed that the TGA of a mixture of equivalent amounts of -[MeHSiNH]$_x$- and -[MeHSiO]$_x$- would give an average ceramic yield for the two polymers.

Figure 3 shows the TGA data for pure -[MeHSiNH]$_x$-, -[MeSi(O)$_{1.5}$]$_x$-, and a 1:1 molar mixture of -[MeHSiNH]$_x$- and -[MeHSiO]$_x$- treated with Cp_2TiMe_2. The 900°C ceramic yield for pure -[MeHSiNH]$_x$- is 37% as expected for this molecular weight[9]. The 900°C ceramic yield for -[MeSi(O)$_{1.5}$]$_x$-, produced by Cp_2TiMe_2 catalyzed polymerization of -[MeHSiO]$_x$-, averages about 76-80%. The numerical average expected from a 1:1 equimolar mixture of the two would be 56-58%. As seen in Figure 3, the catalytically transformed 1:1 equimolar mixture gives a polymer with a ceramic yield of approximately 74-76%, which is contrary to what is expected. In fact, it suggests that in the presence of the siloxane, the catalyst is now able to polymerize the polysilazane. To test this possibility and to determine whether or not we could make a range of copolymeric mixtures, we attempted to copolymerize various ratios of -[MeHSiNH]$_x$- (SiMe) to -[MeHSiO]$_x$- (SiO).

Insert Figure 3

Table 1 records the ceramic yields for 1:1, 3:1, 9:1 and 19:1 molar ratios of SiMe to SiO. These yields all differ from the ceramic yield of pure

SiMe polysilazane. We conclude that we have found an approach to polymerizing the SiMe alone. One simply needs a certain amount of the hydridosiloxane, which probably generates the active ligand/catalyst. We are currently attempting to determine the lower limit of hydridosiloxane required to generate the true active SiMe polymerization catalyst and to independently synthesize the catalyst.

Given that SiMe is the major component in all but the 1:1 version, these results indicate that we can successfully copolymerize the two preceramics. Tables 1 and 2 list the apparent ceramic compositions following pyrolysis of the preceramics to 900°C in N_2. The apparent ceramic compositions reported in Table 1 are based on the assumption that pyrolysis of the copolymers leads to the formation of the ceramic products normally found for the individual preceramics. Table 2 lists apparent ceramic compositions that are calculated on the assumption that silicon oxynitride is formed as the major ceramic product.

SiMe:SiO	Ceramic Yield (wt %)	Si_3N_4	SiC	SiO_2	C
0:1	78	--	19	70	10
1:0	37	65	24	--	10
1:1	72	31.3	19.7	38.2	10.4
3:1	62	43.1	19.8	26.7	9.9
9:1	61	52.8	22.1	14.2	10.1
19:1	61	62.0	19.4	7.3	10.7

Table 1. Apparent Ceramic Compositions for Copolymers of SiMe and SiO Assuming That Si_2ON_2 Does Not Form. Apparent compositions based on silicon as the limiting element. Precursors pyrolyzed to 900°C in N_2.

SiMe:SiO	Si$_2$ON$_2$	Si$_3$N$_4$	SiC	SiO$_2$	C
1:1	44.7	0.0	19.7	24.8	10.4
3:1	61.6	0.0	19.9	8.2	9.9
9:1	47.5	19.6	22.1	0.0	10.1
19:1	24.3	45.0	19.4	0.0	10.7

Table 2. Apparent Ceramic Compositions for Copolymers of SiMe and SiO Assuming That Si$_2$ON$_2$ Forms. Apparent compositions based on silicon as the limiting element. Precursors pyrolyzed to 900°C in N$_2$.

Because the 900°C ceramic products we obtain for the SiMe/SiO preceramic mixtures are amorphous, it has not been possible to use x-ray powder diffractometry to determine whether their apparent ceramic compositions are best represented by those listed in Table 1 or Table 2. Furthermore, heating to higher temperatures, to obtain crystallization, will surely lead to formation of Si$_2$ON$_2$; therefore, use of this characterization method would be invalid.

The DRIFTS spectra for the 1:1 mixture, Figure 4, offer some insight into what is probably occuring in the polymerized species. Comparison

Insert Figure 4

with the spectra in Figures 1 and 2 shows some substantial differences especially at the 600 to 800°C range. There is one especially large peak at approximately 1780 cm^{-1}. We submit that this may be an amido v C=O peak; however, it is too early to tell. We believe that the set of spectra shown in Figure 4 are distinctly different from an overlay of the spectra found in Figures 1 and 2; therefore, we suspect that segregation is not maintained even at temperatures as low as 600°C and the copolymer system is likely to be a useful precursor to Si$_2$ON$_2$ but is probably not a useful model of a block or graft copolymer.

One important observation made in these studies is that under some

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conditions it is possible to use a titanium based catalyst to polymerize the SiMe polysilazane at room temperature We are pursuing this system as an alternative to the ruthenium based catalysts we have used until recently[7].

3. Acknowledgements

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Captions for Figures

Figure 1. DRIFT Spectra for Samples of -[MeSi(O)$_{1.5}$]$_x$- Pyrolyzed Under N$_2$ to Various Temperatures. Precursor prepared by reaction of -[MeHSiO]$_x$- (M$_n$ ≈ 2000 D) with Cp$_2$TiMe$_2$, 0.1 wt percent catalyst at room temperature.

Figure 2. DRIFT Spectra for Samples of -[MeHSiNH]$_x$- Pyrolyzed Under N$_2$ to Various Temperatures. Precursor prepared by reaction of -[MeHSiNH]$_x$- (M$_n$ ≈ 600 D) with Ru$_3$(CO)$_{12}$, 0.1 wt percent catalyst at 40°C for 48 h.

Figure 3. Thermogravimetric Analysis of -[MeSi(O)$_{1.5}$]$_x$- (a), -[MeHSiNH]$_x$- (c) and a 1:1 Copolymer of -[MeHSiNH]$_x$- and -[MeSi(O)$_{1.5}$]$_x$- (b). Pyrolyzed Under N$_2$ at a Heating Rate of 5°C/min. SiO precursor and SiMe/SiO copolymer precursor prepared by reaction of -[MeHSiO]$_x$- or a -[MeHSiO]$_x$-/-[MeHSiNH]$_x$- mixture with Cp$_2$TiMe$_2$, 0.1 wt percent catalyst at room temperature.

Figure 4. DRIFT Spectra for Samples of SiMe/SiO Copolymer Precursor Pyrolyzed Under N$_2$ to Various Temperatures. Precursor prepared by reaction of a 1:1 equimolar -[MeHSiO]$_x$-/-[MeHSiNH]$_x$- mixture with Cp$_2$TiMe$_2$, 0.1 wt percent catalyst at room temperature.